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CALCULATION OF THE OPTIMAL FIRING REGIMES FOR CERAMICS BASED ON ZIRCONIUM AND ALUMINUM DIOXIDE

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An approach to obtaining ceramic in the system ZrO_2 - Al_2O_3 with high physical-mechanical indices and low sintering temperature based on theoretical calculated optimal firing regimes is examined. The calculation is performed taking account of the kinetic parameters of the sintering process.

Key words: zirconium dioxide, corundum, eutectic additive, kinetics of sintering, sintering temperature, mechanical strength, optimization, firing regime.

Even though new types of materials necessary for particular problems have been added to the materials base, the search for real solutions is not over. This is largely due to the change in the areas of application or conditions of operation of particular articles and equipment. Owing to their unique physical and technical properties ceramic materials are practically ubiquitous. In addition, considering their high mechanical strength, crack resistance, durability, hardness, and chemical stability ceramics based on the system ZrO_2 – Al_2O_3 are most promising [1, 2].

Strong and viscous ceramic in the system ZrO₂–Al₂O₃ was first obtained by Claussen. At present this system is the object of most research owing to the high modulus of elasticity of Al₂O₃ (up to 400 GPa), which makes it possible to create significant stresses on ZrO₂ inclusions and is most conducive to keeping ZrO₂ in the tetragonal phase. In addition, for Al₂O₃ and ZrO₂ there is virtually no mutual solubility at high temperatures, which is also conducive for realizing phase hardening. The transformation hardening of the composite ZrO₂–Al₂O₃ intensifies as the uniformity of the ZrO₂ distribution increases. A nonuniform distribution of zirconium dioxide results in larger grains of the components and reduced strength. Zirconium dioxide can be maintained in the tetragonal modification either by introducing small quantities of stabilizing additives or by decreasing the particle size.

The second method is considered to be preferable, because at high temperature the additives can diffuse into the matrix.

The system $\rm ZrO_2$ – $\rm Al_2O_3$ is fundamental for an entire series of structural materials. Specifically, it is promising for fabricating the friction pairs of a cutting tool [3]. In domestic practice hard-metal cutting materials (for example, VK-8) are often used for such tools. The cutting edge of a ceramic tool is thinner (0.1 – 0.2 μ m compared with 0.7 – 0.8 μ m for metal) and its service life is 7 – 10 times longer without regrinding; it also affords a high cutting rate. As a rule, the ultimate strength in bending of such a ceramic is at least 800 MPa.

Even though ZrO₂-Al₂O₃ ceramic has been studied quite well the problems associated mainly with high resource- and energy-intensiveness of the technology used for obtaining such materials remain topical. For this reason it is important to develop a more effective method of regulating the microstructure of ceramic with high physical and mechanical properties, formed during the firing process, as well as lowering the production costs and increasing the quality of the finished product. One promising way to solve this problem is to use as modifiers additives of eutectic compositions making it possible to lower the sintering temperature to values accessible in furnaces with silicon carbide heaters [4]. In addition, it is important to develop an optimal regime for firing the ceramic in order to be able to efficiently regulate the microstructure of the material obtained and synthesize a dense ceramic. The firing regime is one of the main conditions determining the creation of directly linked structures, which largely determines the high physical and mechanical properties of ceramics.

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Modifier	Con	mponent conte	nt, %	$t_{ m melt}$, °C	[MO]	$\frac{[Al_2O_3]}{[RO_2]}$,
cation	MO	Al_2O_3	SiO ₂ (TiO ₂)		$[RO_2]$		A
Mn ²⁺	28.96	12.77	58.27	1140	0.50	0.23	0.73
Ca^{2+}	64.23	27.94	7.83	1335	8.20	3.57	11.77
Mn^{2+}	32.00	0.00	(68.00)	1290	0.47	0.00	0.47
Ca ²⁺	26.00	10.00	(64.00)	1390	2.60	0.16	2.76

TABLE 1. Values of the Coefficient A for the Eutectic Additives Used in the Work

Notations: t_{melt} is the melting temperature; $A = \frac{[MO]}{[RO_2]} + \frac{[Al_2O_3]}{[RO_2]}$.

The principles for choosing additives forming the liquid phase during sintering were formulated on the basis of data confirmed in practice, viz., data obtained in [5]:

- 1) equality of the coordination numbers of the aluminum ion in melt and the refractory phase, which is attained by regulating the acidity of the low-melting component, picking a modifier ion with the optimal ionic potential, as well as technological techniques, for example, firing in a regulated atmosphere;
- 2) using additives possessing the optimal temperature of appearance of the liquid phase in a multicomponent system;
- 3) wetting the surface of the solid phase with a eutectic melt;
 - 4) minimal viscosity of the melt;
 - 5) high surface tension of the melt;
- 6) taking account of the geometry and electrostatic state of the interface of solid and liquid phases.

One of the main problems is that the eutectics formed must be able to destroy the structure of the silicon anions (in general, an acidic oxide, including titanium oxide, zirconium oxide, and others), which will decrease the viscosity and increase the transport properties of the liquid. Thus, the eutectic must contain an adequate amount of modifier anions M with a relatively low content of aluminum cations [6, 7].

If there are too many aluminum cations, then because it is amphoteric the aluminum starts to manifest acidic properties, isomorphically replace silicon in the silicon-oxygen tetrahedra, and form large complex anions. In this case the aluminum cation no longer transfers mass, and the sintering process will be more complicated or absent completely. The aluminum cation will start to from the complexes AlO_4^{5-} .

At the same time it is known for the example of aluminum-oxide materials and materials in the system Al_2O_3 – ZrO_2 (the latter to $30\%^6$) that such systems sinter effectively under the conditions of an acidic liquid phase. Therefore, under these conditions silicon (titanium) oxide manifests acidic properties and aluminum oxide basic properties, which it will manifest in the coordination state AlO_6^{9-} .

Thus, it is necessary to limit the amount of the cations M, which can be determined from the molar ratio $\frac{[MO]}{[RO_2]}$. The

smaller this ratio (but not zero; pure silicon possesses poor transport properties), the more efficient sintering is. Therefore, on this basis, the content of the cations M in the melt must be optimal (for the sintering process to occur). Their minimal content in the liquid is a prerequisite for the silicon-oxygen tetrahedra to form a three-dimensional network; the maximum content predetermines the basic properties of the melt.

The number of aluminum ions in a eutectic melt can be estimated from the molar ratio $\frac{[Al_2O_3]}{[RO_2]}$. The smaller this ra-

tio, the higher the probability of finding an aluminum ion in coordination +6 is.

Thus, a criterion for determining the capacity of the liquid phase to form densely sintering materials is the coefficient $A = \frac{[MO]}{[RO_2]} + \frac{[Al_2O_3]}{[RO_2]}$. The smaller the value, the more

efficiently the additive works.

It is known that all additives of the eutectic type can be divided into a number of groups, of which the most effective are the aluminum-silicate and aluminum-titanate ones. It is also known that additives containing the cations of p- and d-elements promote sintering the most [6-8]. For this reason, the following additives were used as modifying additives making it possible to significantly lower the sintering temperature: MnO–TiO₂ (MnO–Al₂O₃–TiO₂); MnO–Al₂O₃–SiO₂; CaO–Al₂O₃–TiO₂; and, CaO–Al₂O₃–SiO₂.

The values of the coefficient A for the experimental additives are presented in Table 1.

Thus, from the standpoint of the criterion under consideration (according to the value of the coefficient A) the additives must be arranged in the following series according to the decrease in the efficiency:

$$\begin{array}{l} {\rm MnO-TiO_2 \rightarrow MnO-Al_2O_3-SiO_2 \rightarrow} \\ {\rm CaO-Al_2O_3-TiO_2 \rightarrow CaO-Al_2O_3-SiO_2}. \end{array}$$

This hypothesis was checked in practice.

⁶ Here and below the content by weight, wt.%, unless otherwise stipulated.

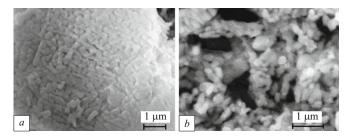


Fig. 1. Photographs of the microstructure of PSZD powder obtained by stabilizing with a hydrosol of yttrium: a) cooled; b) calcined; magnification on photographs: a) ×25,000; b) ×35,000.

The initial materials and additives were prepared as follows.

To stabilize $\rm ZrO_2$ a hydrosol of yttrium hydroxide was added to zirconium hydroxide 3 mol.%; the pH of the suspension was regulated by a water solution of ammonia. The composition obtained was mixed with acetone and disaggregated in a Teflon drum with corundum balls. The suspension was dried at 80°C, and the powder was passed twice through a capron sieve with 0.5 mm cells and then calcined at 500°C. The synthesized powder was comminuted in acetone in a vibratory mill and dried at 80°C. The material obtained is a tetragonal solid solution based on zirconium dioxide (partially stabilized zirconium dioxide (PSZD)). Petrographic analysis showed the size of the crystals of the solid solution to be $\ll 1 \mu m$ (Fig. 1).

Magnesium carbonate was introduced into the aluminum hydroxide; the material was comminuted by the wet method using aluminum oxide balls in a corundum drum. The suspension was dried at 80° C, after which the powder was calcined at 1300° C. The calcined material was comminuted by the wet method under the same conditions as before calcination. The suspensions were dried at 80° C, and the powder was passed through a $0.5~\mu m$ sieve and used to make the compositions. Petrographic analysis showed the corundum crystals to be $0.5-1.5~\mu m$ in size (Fig. 2).

The compositions of the additives used in this work are presented in Table 2.

To make the additives the mixtures of the initial materials with nominal composition were comminuted with corundum balls in a ball mill. The suspensions obtained were dried at temperature 80°C. The comminuted powders of the addi-

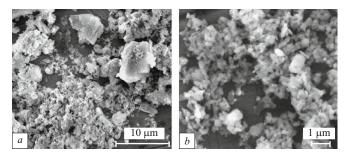


Fig. 2. Photographs of Al_2O_3 powder obtained from aluminum hydroxide. Magnification: $a) \times 5000$; $b) \times 20,000$.

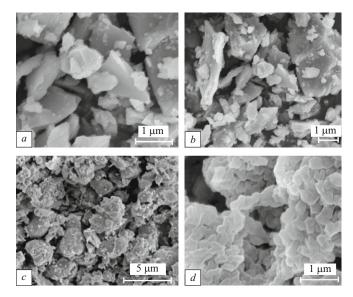


Fig. 3. Photographs of the microstructure of the powders of the synthesized eutectic additives of the systems: a) MnO–TiO₂; b) MnO–Al₂O₃–SiO₂; c) CaO–Al₂O₃–TiO₂; and, d) CaO–Al₂O₃–SiO₂.

tives with the compositions CaO–Al₂O₃–SiO₂, CaO–Al₂O₃–TiO₂, and MnO–TiO₂ were calcined (synthesized) at temperature 1000°C, and the additive with composition MnO–Al₂O₃–SiO₂ at temperature 700°C. The calcined materials were comminuted under the same conditions as before synthesis. The temperature regimes were chosen according to the petrographic studies and x-ray phase analysis. The ready powders were used for making the compositions. Photographs of the microstructure of the additives are presented in Fig. 3.

TABLE 2. Composition of the Eutectic Additives Used and Their Melting Temperatures t_{melt}

A 1114:	Additive des-		- t °C				
Additive	ignation	Al_2O_3	SiO_2	CaO	MnO	${\rm TiO_2}$	$-t_{\mathrm{melt}}$, °C
MnO–TiO ₂	MT	_	_	_	35	65	1290
$MnO-Al_2O_3-SiO_2$	MAS	19.0	51.0		30	_	1140
CaO-Al ₂ O ₃ -TiO ₂	CAT	13.0	_	19.0	_	68	1390
CaO-Al ₂ O ₃ -SiO ₂	CAS	27.9	7.9	64.2	_	_	1335

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	Properties of ceramics with MT additive content, %*								
t_{fire} , °C	2.0		3.0		4.0		5.0		
	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %	
1400	5.17	0.2	5.18	0.0	5.19	0.0	5.20	0.0	
1450	5.19	0.0	5.19	0.0	5.20	0.0	5.20	0.0	
1500	5.19	0.0	5.20	0.0	5.22	0.0	5.24	0.0	
1550	5.15	0.7	5.15	0.7	5.16	0.6	5.17	0.6	

TABLE 3. Ceramic Properties of Samples based on PSZD, Containing 20%* Al₂O₃, with MnO-TiO₂ (MT) Additives

TABLE 4. Ceramic Properties of Samples Based on PSZD, Containing 20%* Al₂O₃, with MnO–Al₂O₃–SiO₂ (MAS) Additives

	Properties of ceramics with MAS additive content, %*									
$t_{\rm fire}$, °C	2.0		3.0		4.0		5.0			
	ρ , g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %		
1400	4.90	7.3	4.99	4.5	5.01	4.0	5.01	3.7		
1450	5.03	2.9	5.08	1.5	5.11	0.5	5.11	0.4		
1500	5.11	1.0	5.16	0.7	5.19	0.0	5.20	0.0		
1550	5.16	0.5	5.18	0.3	5.20	0.0	5.22	0.0		

^{*} Content by weight, %.

TABLE 5. Ceramic Properties of Samples Based on PSZD, Containing $20\%^*$ Al₂O₃, with CaO-Al₂O₃-TiO₂ (CAT) Additives

	Properties of ceramics with CAT additive content, %*									
$t_{\rm fire},{}^{\circ}{\rm C}$	2.0		3.0		4.0		5.0			
	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %		
1400	4.92	10.1	4.92	9.9	4.91	9.7	4.90	9.6		
1450	5.12	2.0	5.11	2.0	5.09	1.9	5.08	1.8		
1500	5.19	0.0	5.18	0.0	5.18	0.0	5.17	0.0		
1550	5.17	0.2	5.17	0.2	5.16	0.1	5.15	0.1		

^{*} Content by weight, %.

The prepared additives were introduced into prepared mixtures of $\rm ZrO_2$ and $\rm Al_2O_3$. The mixing was accomplished in Teflon drums by corundum balls. The prepared suspensions were dried at temperature $80^{\circ}\rm C$.

The samples in the form of $40 \times 6 \times 4$ mm bars were formed by means of semidry pressing under pressure 100 MPa.

The firing was conducted in the temperature range 1250 – 1550°C. The rate of heating was 3.0 K/min with 3 h soaking at the final temperature. To investigate the sintering kinetics by a nonisothermal method [9] the firing was con-

ducted in the temperature interval 1250 - 1500°C. The rates of heating were 1.5 and 3.0 K/min.

The results were used as a basis for determining the optimal amounts of the eutectics introduced and the kinetic parameters of the sintering process (order of the reaction, apparent energy of activation).

The properties of the samples with eutectic additives in the systems $MnO-TiO_2$, $MnO-Al_2O_3-SiO_2$, $CaO-Al_2O_3-TiO_2$, and $CaO-Al_2O_3-SiO_2$ are presented in Tables 3-6.

In the system with the modifier $MnO-TiO_2$ zero open porosity P_0 is obtained at firing temperature 1450°C with ad-

^{*} Content by weight, %.

	Properties of ceramics with CAS additive content, %*									
t_{fire} , °C	2.0		3.0		4.0		5.0			
	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %	ρ, g/cm ³	P ₀ , %		
1400	4.96	4.0	4.94	5.3	4.92	7.0	4.85	11.8		
1450	5.07	1.9	5.05	2.3	5.03	3.5	4.97	7.2		
1500	5.14	0.5	5.13	0.6	5.12	0.6	5.11	0.7		
1550	5.17	0.2	5.17	0.1	5.17	0.0	5.16	0.0		

TABLE 6. Ceramic Properties of Samples Based on PSZD, Containing 20%* Al₂O₃, with CaO–Al₂O₃–SiO₂ (CAS) Additives

ditive content 2.0%. A subsequent increase of the amount of eutectic does not greatly improve the sintering indices (Table 3).

Ceramic with $MnO-Al_2O_3-SiO_2$ modified is characterized by full sintering at 1500°C and additive content 4.0% (Table 4).

For the case of material modified by the eutectic CaO– Al_2O_3 – TiO_2 , the maximum values of the properties were obtained at temperature 1500°C and additive amounts 2.0 and 3.0% (Table 5). Since the properties of the samples are not observed to improve with increasing additive content, the optimal amount of CaO– Al_2O_3 – TiO_2 must be 2.0%.

Similar studies were performed for a system with the additive $CaO-Al_2O_3-SiO_2$. In this case zero open porosity P_0 and average density $\rho = 5.17$ g/cm³ are attained at temperature 1550°C and additive content 4.0% (Table 6).

The optimal amounts found for the additives were used for subsequent investigations.

The general sintering mechanisms for the materials were determined. Two mechanisms were found to predominate. At low temperatures the order of the reaction n < 1 (n = 0.5 was obtained for the additive MnO–TiO₂; n = 0.6 for MnO–Al₂O₃–SiO₂; n = 0.3 for CaO–Al₂O₃–TiO₂; n = 0.6 for CaO–Al₂O₃–SiO₂). At high temperatures the reaction order n > 1 (n = 6.7 for MnO–TiO₂; n = 5.4 for MnO–Al₂O₃–SiO₂). n = 1.2 for CaO–Al₂O₃–TiO₂; n = 5.4 for CaO–Al₂O₃–SiO₂).

The apparent activation energy of sintering was determined to be 250 kJ/mole for ceramic with MnO–TiO $_2$ additive, 280 kJ/mole for MnO–Al $_2$ O $_3$ –SiO $_2$, 320 kJ/mole for CaO–Al $_2$ O $_3$ –TiO $_2$ for 320 kJ/mole, and 350 kJ/mole for CaO–Al $_2$ O $_3$ –SiO $_2$.

The thermodynamic calculations show that for all eutectic additives, aside from the formation of a bond between ZrO₂ and Al₂O₃, a direct bond must be formed between the ZrO₂ grains and between the Al₂O₃ grains, which makes it possible to realize the principle of the creation of direct-bonded structures. The result of the realization of such a mechanism of sintering for ceramic containing a eutectic additive in the system MnO–TiO₂ is presented in Fig. 4.

The basic kinetic parameters can be used to develop rational firing regimes for the articles. Introducing the dimen-

sionless parameter Z, characterizing the shrinkage at temperature T,

$$Z=1-\alpha$$
,

where α is the relative shrinkage and assuming that in the firing process

$$Z_0 \ge Z \ge Z_{\text{max}}$$
 and $T_{\text{max}} \ge T \ge T_0$,

where Z_0 is the parameter Z at the minimal temperature of the experiment T_0 and Z_{\max} is the parameter Z at the maximum temperature of the experiment T_{\max} , the firing temperature T for the material is given by

$$T = \frac{\frac{E}{nR}}{\frac{E}{nRT_{\text{max}}} + \ln\left[\frac{Z_0}{Z_{\text{max}}} - k_0 \exp\left(-\frac{E}{RT_{\text{max}}}\right)Z_{\text{max}}^{n-1}\tau\right]},$$

where E is the apparent activation energy, R is the universal gas constant, k_0 is the pre-exponential factor, and τ is the duration of the process.

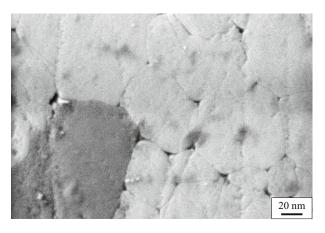


Fig. 4. Photograph of the microstructure of a polished surface of samples containing the eutectic additive MnO–TiO₂: etching with boiling orthophosphoric acid; magnification ×100,000.

^{*} Content by weight, %.

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TABLE 7.	Applicability of the Equation for Calculating the Te	m-
perature for	Developing Efficient Firing Regimes	

	Computational dependence of the	Ultimate strength in bending of ceramic, MPa, annealed according to the regimes				
Additive	interval of firing temperatures $T_{\text{max}} \ge T \ge T_0$	experimental	computational			
MT	$T_{\text{max}} = \frac{9.58 \times 10^7}{\tau_{\text{max}}}$	850 ± 42	900 ± 25			
MAS	$T_{\text{max}} = \frac{8.89 \times 10^7}{\tau_{\text{max}}}$	750 ± 38	810 ± 26			
CAT	$T_{\text{max}} = \frac{11.55 \times 10^7}{\tau_{\text{max}}}$	700 ± 28	740 ± 24			
CAS	$T_{\text{max}} = \frac{11.20 \times 10^7}{\tau_{\text{max}}}$	600 ± 30	650 ± 24			

This equation makes it possible to calculate the temperature regime for which the sintering process is uniform and as fast as possible. The computation results obtained with this relation in comparison with the experimental data are presented in Table 7.

Equations making it possible to design rational regimes for firing articles so that the sintering process is uniform and proceeds as rapidly as possible were proposed on the basis of calculations of the sintering mechanisms for ceramics in the system ZrO_2 – Al_2O_3 .

The adequacy of these equations was confirmed experimentally. In summary, for technological practice it is important to calculate the sintering mechanisms on the basis of data obtained by the means of non-isothermal kinetics.

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